SEPP21.001C1 PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	:	Tois et al.
Appl. No.	:	10/678,766
Filed	:	October 2, 2003
For	:	METHOD OF GROWING OXIDE THIN FILMS
Examiner	:	Matthew J. Song
Group Art Unit	:	1722

DECLARATION OF SUVI HAUKKA UNDER 37 C.F.R. § 1.132

Dear Sir:

I, Suvi Haukka, do hereby declare and say as follows:

1. I am currently employed as an Executive Scientist for ALD applications for ASM Microchemistry Oy, in Helsinki, Finland. For the past nineteen years I have worked in various capacities including Research Scientist, Catalyst Technology Manager, Process Development Manager and R&D Manager which all have been related to atomic layer deposition (ALD). In particular, my work has focused on ALD and applications of it for semiconductor equipment, processes, and devices as well as development of ALD apparatus. Over the course of my career, I have been an author on over 60 scientific papers, primarily concerning ALD processes, applications and apparatus. In addition, I am an inventor of more than 60 patents and patent applications in the field of semiconductor fabrication. I am also listed as an inventor on the present patent Application. In 1994 I earned a Doctor of Philosophy degree from Laboratory of Analytical Chemistry, University of Helsinki, Finland.

2. I have read and understand the claims in the present patent application. I understand that the claims concern processes for producing a thin metal silicon oxide ($MSiO_x$) film on a substrate comprising contacting a substrate with a vapor phase silicon compound, contacting the substrate with a vapor phase metal compound, and converting adsorbed

compounds on the substrate into $MSiO_x$ by contacting them with a reactive vapor phase oxygen source, in the manner recited in independent Claims 1, 22 and 36, and adsorbing a layer of a silicon compound on a substrate in a flow type reactor, adsorbing a layer of a metal compound on a substrate, and converting the adsorbed compounds into a tertiary metal silicon oxide by contact with a reactive vapor phase oxygen source compound, in the manner recited in independent Claim 24.

3. I am familiar with the course of prosecution of the present patent application, including the Office Action mailed on November 18, 2008, in which George et al. ("Surface Chemistry for Atomic Layer Growth"), Sandhu et al. (U.S. Patent No. 6,313,035), Leskela et al. (Journal De Physique IV) and Suntola et al. (U.S. Patent Nos. 6,015,590) were discussed. I understand that the Examiner concluded that the skilled artisan would understand George et al. read in conjunction with Sandhu et al., Leskela et al. and Suntola et al. to render obvious ALD processes for producing metal silicon oxide films as claimed. For the reasons detailed below, I disagree with this conclusion.

4. As an expert in the field of semiconductor fabrication, I had an understanding of the scientific and engineering principles applicable to equipment for thin film deposition, particularly for CVD and ALD, at the time the present application was filed.

5. Independent Claims 1, 22, 24 and 36 have been currently amended to recite a 'flow type reactor.' It is my opinion that at the time of the invention, the ordinary engineer would have understood a 'flow type reactor' as a reactor in which reactants and/or inert gases are separately flowed through the reactor during the ALD deposition cycle where the reactor is continuously pumped. This is in contrast to a reactor that has its outlet closed during reactant pulses in order to 'soak' the substrate in the reactant for prolonged periods.

6. George et al. does not teach a 'flow type' reactor but a 'backfill' reactor, which operates by closing the exhaust and allowing reactants to fill the reactor and contact a substrate over the course of long exposure times. Consistent with this, George et al. teaches that substrates were exposed to $SiCl_4$ and H_2O for SiO_2 growth for as long as 72 minutes, and to TMA and H_2O for Al_2O_3 growth for as long as 200 seconds. (Figures 2-4 and 7-8, page 13123-13124).

7. I would not have expected the process for depositing SiO_2 disclosed in George et al. to work in a flow type reactor. Instead, I would have understood that the reaction between $SiCl_4$ and H_2O is kinetically slow, and that long reaction times in a closed system would be necessary to achieve growth of SiO_2 films. Again, consistent with this, George et al. teaches that long exposure times of several minutes were used to achieve SiO_2 growth from $SiCl_4$ and H_2O. (Figure 2-4, page 13123). The teachings of George et al. would have indicated to a skilled artisan at the time of our invention that full surface reactions require the long and undisturbed reactant exposure provided by 'backfill' reactors.

8. It is also my opinion that the skilled artisan would not have expected commercially viable growth of a metal silicon oxide film in a flow type reactor, based on the lack of appreciable SiO_2 growth in a flow type reactor, and the growth rates that were experimentally observed in a flow type reactor for individual metal oxides, as described below.

9. For example, we found that slow or no SiO_2 film growth occurs by ALD in a flow type reactor using conventional silicon precursors. In particular, we found that using $SiCl_4$ and H_2O does not produce appreciable SiO_2 film growth by ALD in a flow type reactor. These results have been submitted by my co-inventor Marko Tuominen in a Declaration to the United States Patent and Trademark Office dated November 29, 2007, for related Application No. 10/148525. (*See* paragraph 8 of the attached Tuominen Declaration and attached experimental results).

10. The low growth rates of single metal oxides have also been highlighted to the Examiner in a table, reproduced below, comparing the growth rates of metal silicon oxides and their respective metal oxides, in Applicants' Response to Final Office Action, mailed October 31, 2007. As noted on page 8 of the Response, the following growth rates were reported in the literature for single metal oxides (other than SiO_2) deposited by ALD using the listed metal precursors. I confirm that we observed the growth rates for the metal silicon oxides and the silicon oxide listed in the table by ALD using the same metal precursors in a flow type reactor.

The differences between the sum of the listed growth rates for the metal oxide and silicon oxide, and the growth rate for the corresponding metal silicon oxide, were not expected:

Oxide	Growth Rate Å/c	Metal Silicon Oxide	Growth Rate Å/c
TiO_2 from $TiCl_4$	0.5	$SiTiO_x$	0.9
Ta_2O_5 from $TaCl_5$	0.43	$SiTaO_x$	1.1
HfO_2 from $HfCl_4$	0.5	$SiHfO_x$	1.23
ZrO_2 from $ZrCl_4$	0.5	$SiZrO_x$	1.1
La_2O_3 from $La(thd)_3$	0.36	$SiLaO_x$	0.75
Y2O_3 from $Y(thd)_3$	0.23	$SiYO_x$	0.73
SiO_2 from AMTMS	0.2		

11. George et al. also teaches HfO_2 deposition from $HfCl_4 + H_2O$ and SiO_2 deposition from $SiCl_4 + H_2O$. (Page 13122). As discussed above, we have found experimentally that while George et al. was able to achieve SiO_2 growth in their closed system, there is no appreciable growth of SiO_2 from $SiCl_4$ and H_2O in a flow type reactor. We have also found HfO_2 can be grown in a flow type reactor from $HfCl_4$ and H_2O with a growth rate of about 0.5 Å/cycle. Even if the teachings of George et al. about single oxide depositions using long exposure times in a 'backfill' reactor were relied on, prior to the present invention I would not have expected it to be possible to incorporate SiO_2 in HfO_2 to form hafnium silicate by using $HfCl_4 + H_2O$ and $SiCl_4 + H_2O$ processes in a flow type reactor, because SiO_2 does not grow appreciably in a flow type reactor.

12. Surprisingly, and contrary to what was expected, we have found that hafnium silicate grows very well by using $HfCl_4 + H_2O$ and $SiCl_4 + H_2O$ in a flow type reactor. Hafnium silicate films made by using a 1:1 (HfO_2):(SiO_2) cycle ratio from $HfCl_4 + H_2O$ and $SiCl_4 + H_2O$ comprised about 9-13 at-% of silicon, about 15-19 at-% of hafnium and 69-72 at-% of oxygen, as measured by Electron Spectroscopy for Chemical Analysis (ESCA), which is also known as X-ray photoelectron spectroscopy (XPS), after sputtering the contaminants from air. The results of this analysis are submitted with this Declaration. Moreover, the specification of related Application No. 11/868,333 also provides further evidence that hafnium silicate can be grown using $HfCl_4$, $SiCl_4$ and H_2O as precursors in a flow type reactor (Pulsar® reactor manufactured by ASM America, Inc.). (*See* Application No. 11/868,333, pages 12-15).

13. Thus we have found that while SiO_2 grows slowly or not at all on SiO_2 surfaces in a flow type reactor, it grows very well when there is a metal oxide surface on the substrate, which affects the silicon precursor reaction on the growing surface. Again, achieving growth of a metal silicon oxide film in a flow type reactor was unexpected because the skilled artisan would not have expected any appreciable silicon oxide, a component of the metal silicon oxide, to grow on the substrate in a flow type reactor.

14. Prior to the invention, the ordinary engineer would have expected the growth rate of a metal silicon oxide to be equal to the growth rate of its corresponding metal oxide and the growth rate of silicon oxide. However, not only did we surprisingly find that metal silicon oxides can be grown in a flow type reactor, we have also unexpectedly found that the growth rate for metal silicon oxides in a flow type reactor is much higher than the sum of the growth rate of metal oxide and the growth rate of silicon oxide, which would have been the expected growth rate for the metal silicon oxide.

15. We have unexpectedly found that the growth rate for metal silicon oxides in a flow type reactor is even higher than what one would have expected by combining the growth rates of the individual oxides from which the metal silicon oxide is formed. For example, we have found a growth rate of about 0.5 Å/cycle for HfO_2 (using $HfCl_4$) and in the range of about 0.16 to about 0.2 Å/cycle for SiO_2 (using 3-aminopropyltrimethoxy silane). Thus, a growth rate in the range of about 0.66 to 0.70 Å/cycle would have been expected for $HfSiO_x$ (using a combination of HfO_2 and SiO_2 reactions). However, a growth rate of 1.23 Å/cycle was achieved instead, which is more than a 75% unexpected increase. (*See* Example 2 of Application). Thus, the growth rate of the metal silicon oxide was even higher than expected from combining the growth rates of the individual oxides from which the metal silicon oxide is formed.

16. In essence, we have observed that a 'boost' in growth rate for metal silicates occurs when there is a metal oxide surface present, which affects the silicon precursor reaction on the growing surface. This 'boost' does not occur in the growth of individual oxides. The increase in silicon precursor reactions in the presence of a metal oxide surface is surprising and was not expected.

17. Example 2 of the Application also reports unexpectedly high growth rates for metal silicon oxides of six different metals. Based on these results, I would conclude that the increase in growth rate for metal silicon oxides over that of each individual oxide from which the metal silicon oxide is formed is a phenomenon that occurs generally for all metal silicon oxides over their respective individual oxides.

18. The Examiner incorrectly believes that complete reactions would be expected produce the maximum growth rate of approximately 1.1 Å/cycle and that Applicants' growth rate of 0.2 Å/cycle represents "incomplete half-reactions." (Final Office Action, page 10). I disagree with the Examiner's allegation. Atomic layer deposition (ALD), or atomic layer epitaxy (ALE) as it is referred to by George, is based on saturated and complete surface reactions of chemicals (that do not decompose on the surface) with reactive surface sites. However, all ALD processes will produce unique growth rates, depending on the particular chemicals used, deposition temperatures and many other factors. The different factors that determine the overall growth rate include, among other things, the size of the precursor molecules, the density of the reactive surface sites (*e.g.*, OH-groups) that determines where the precursor can react on the surface, and all the various stereochemical configurations and molecular arrangements that can occur on the depositing surface. Thus, SiO_2 deposition processes using different silicon precursors or deposition parameters can have very different growth rates. The SiO_2 growth rate we found of about 0.2 Å/cycle does represent that of complete, saturating reactions, and not "incomplete half reactions," as the Examiner has incorrectly alleged. Thus, it is appropriate to compare the growth rates achieved for metal silicon oxides to that of the growth rates of individual oxides in arriving at the conclusion that the growth rate of the metal silicon oxide is surprisingly higher than that expected from the individual oxides.

19. Prior to the present patent application of Tois et al., I was not aware of any process for producing a metal silicon oxide film by contacting a substrate in a flow type reactor with a vapor phase silicon compound, a vapor phase metal compound and a reactive vapor phase oxygen source in the manner claimed in Claims 1, 22 and 36, and adsorbing a layer of a silicon compound on a substrate in a flow type reactor, adsorbing a layer of a metal compound on the substrate, and converting the adsorbed compounds into a tertiary metal silicon oxide by contact with a reactive vapor phase oxygen source compound, in the manner claimed in Claim 24.

20. For the reasons noted above, I would not have modified the disclosures in George et al., Leskela et al. and Suntola et al. to produce metal silicon oxide films on a substrate in a flow type reactor in the manner claimed, much less expect the increase in growth rate observed.

21. Further, I would not have expected the commercially viable results we obtained in producing metal silicon oxide films on a substrate in a flow type reactor in the manner claimed.

22. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Dated: March 31, 2009

By: ____________________

Suvi Haukka

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